

FIA ANALYSIS OF COAL TAR

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Several rapid and simple analytical procedures have been used for coal tar assay; likewise, many long and tedious methods have been worked out. The rapid, simple methods are generally criticized for not giving sufficient information while the long, tedious methods are unpopular because they are just that--long and tedious. The present system is offered as an analytical tool which is neither very tedious nor greatly time consuming but which gives considerable useful information.

The Fluorescent Indicator Adsorption (FIA) method was originally designed for use on light petroleum fractions of a fluid nature. Essentially it consists of displacement adsorption chromatography of hydrocarbon mixtures on a silica gel column, fluorescent indicators being used to detect the zones containing the various chemical types, namely, saturates, olefins, and aromatics.

Adaptation of FIA to Coal Tar

Two major problems were encountered by the Bureau of Mines in adapting this analysis for use on coal tar. First, the tar is often too viscous to flow in a chromatographic column, and second, coal tar contains compounds other than hydrocarbons such as neutral oxygenates, tar acids, and tar bases.

First attempts by the Bureau to chromatograph samples of low-temperature tar were unsuccessful, as the waxes would solidify during fractionation and prevent the movement of the sample in the column. A steam-heated column was constructed, but the silica gel would not absorb at the elevated temperature, and no separation was possible. Attempts were made to remove the waxes by precipitating them from a cold acetone solution of the tar or by extracting them with petroleum ether. Neither system was satisfactory, as it was difficult to establish with any accuracy just how much wax was removed. The problem was finally solved by diluting the tar with a precisely measured amount of petroleum ether; this served to dissolve the waxes and allowed the tar to move freely down the column, and since the amount of petroleum ether added was known, this could be corrected for in the results.

For solution of the second problem, it was necessary to demonstrate that the FIA method could be used to separate nonhydrocarbon materials as well as hydrocarbons, because the nonhydrocarbons make up a large part of the tar. A synthetic mixture, composed of heptane, octene, benzene, acetophenone, and o-cresol, was made up for this demonstration. When this mixture was run using the standard FIA dyed-gel, the hydrocarbons separated in the usual manner; the acetophenone section then took up the pink dye which normally indicates the end of the chromatogram; the cresol section, a light tan color, followed.

Gross tar, distilled to its cracking temperature, separated on the silica gel column into the same number of zones, but the dark color of the neutral-oxygen and tar acid fractions made it impossible to detect visually the boundary between these two zones. When samples from these sections were examined by infrared spectra, however, bands characteristic of ketone and phenolic hydroxy groups were identified.

Attempts to determine tar bases by the FIA method have so far been unsuccessful.

At this stage of development, it became apparent that not all of the tar sample was being eluted. To correct this failure, changes were made in column design, and stronger displacing agents were employed. Eventually a satisfactory charging column was evolved, and pyridine was chosen as the most suitable displacing agent.

It was found that definition of the boundaries between the various groups was far better when gravity flow was used than when the separation was carried out under pressure. The charging column, therefore, was designed to facilitate the flow so that an analysis by this technique could be completed in a reasonable time. By shortening the charging sections and eliminating the usual capillary, highly satisfactory separations were realized in 6 to 8 hours.

Best results have been obtained from distilled tars. Gross, undistilled tar contains polymeric material and heavy pitch which often obscure the top level of the chromatogram. Tar fractions and whole tars distilled to any temperature up to the cracking point give excellent results. If distillation is impractical or undesirable, the tar can be separated from most of the pitch by dissolving in ether and filtering, or the sample can be washed through a silica gel column with low-boiling petroleum ether or heptane until the eluent is clear, then stripped of solvent.

This, then, is the assay system in its current stage of development. The charging tube consists of two sections, each 10 cm. long; the upper section is 12 mm. OD while the lower is 7 mm. OD. These tubes are joined in a smooth taper, and the lower end of the lower section is tapered to fit into 1/8-inch Tygon tubing that is used to attach the measuring tube. The measuring tube is 3 mm. OD and 120 cm. long and is drawn out to a capillary on the lower end. Davison 923 silica gel, which has been activated at 200° C. overnight, is then funneled into the column. Packing the column is most easily done by attaching a vibrator to a ring stand and clamping the column to this stand. The vibrator is run throughout the packing operation, both to aid filling and to insure uniform packing. When the column has filled to the middle of the 7-mm. section, a small amount of dyed gel is added, and then plain silica gel again to bring the level to about the middle of the upper section.

The sample is prepared by placing 2 ml. of petroleum ether into a 10-ml. graduate and adding tar to bring the level of the mixture to the 4 ml. mark. One to two ml. of pyridine are added and the sample is then well mixed. One ml. of this sample mixture is placed directly on the silica gel in the column, and as soon as the sample is completely adsorbed, an additional layer of 2 to 3 cm. of silica gel is placed on top of the column and packed down. Eluent is added and the chromatogram allowed to develop by gravity flow.

When the upper boundary of the sample is well into the measuring tube, the column is placed in a dark room, where it is illuminated with ultraviolet light and the various sections measured with a meter stick. Half of the total length is due to the added petroleum ether and therefore is subtracted from the length of the saturate section. What remains in this section represents the saturates from the tar. The remaining sections are measured, and the length of each section is proportional to the amount of that chemical type present in the tar.

Results from FIA Assay System

Sine this method is not fully developed, it has not been used extensively on specific assay problems; however, in the course of development, some interesting facts have been disclosed. Confirmation of considerable amounts of oxygen-containing material in the neutral oil is of interest. The FIA analysis of a typical neutral oil fraction from lignite tar follows:

FIA ANALYSIS OF A NEUTRAL OIL FRACTION

Boiling 301-304° C.

Saturates, vol. per cent	18.4
Olefins	7.1
Aromatics	53.3
Oxy-compounds	21.2

The maximum oxygen content of this neutral oil is 3 per cent; therefore, it would seem unreasonable to find that 21 per cent of the sample is oxygen-containing compounds. The mean molecular weight, however, is in the order of 200, and if each such molecule contained a single oxygen atom, the oxygen content would be 8 per cent. To bring the oxygen content to 3 per cent, 350-gram atoms of oxygen-free material must be assumed, for a total of 550-gram atoms. Of this, 36-weight per cent is oxygen-containing material. From this we can see that 21 per cent oxygen-containing neutral compounds in a sample containing 3 per cent oxygen is not at all unreasonable.

Several assays, including cuts from various temperature ranges as well as those distilled over the full boiling range, have been made on distilled fractions of gross tar. Further refinements are necessary before the method can be fully evaluated for this purpose, but there is little doubt that the FIA analysis can be used to differentiate between various tars and to give a good estimate of the chemical types they contain. As an example, the comparative analyses of tars obtained from a North Dakota and a Texas lignite follow.

FIA ASSAY OF TWO GROSS TARS

(Boiling 80-360°)

	North Dakota Tar	Texas Tar
Saturate, vol. per cent	15.1	16.7
Olefins	7.6	10.1
Aromatics	29.7	34.9
Oxy-compounds (neutral + acid)	48.4	38.4

Future Problems

Foremost among the remaining problems is that of distinguishing the boundary between neutral oxy-compounds and tar acids. The boundary is easily observed in very light-colored samples but is completely obscured in the dark color of most tars.

Another desirable development would be a more rapid analysis, particularly for control work. Any speedup would almost certainly result in loss of accuracy, although this loss could be minimized to a tolerable level in most cases. At present, the average run takes about 6 hours.

Eventually, if the system is to be completely general, means must be found to determine tar bases.

- (1) ASTM. Tentative Method of Test for Hydrocarbon Types in Liquid Petroleum Products (Fluorescent Indicator Adsorption (FIA) Method). ASTM D 1319-58T (1954); Revised 1955, 1956, 1958.
- (2) CRIDDLE, D. W., AND LETOURNEAU, R. L. Fluorescent Indicator Adsorption Method for Hydrocarbon-Type Analysis. Anal. Chem. 23, 1620-4 (1951).